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(54) **Supporter for fuel cell, method of preparing same, and electrode for fuel cell, membrane-electrode assembly for a fuel cell, and fuel cell system including same**

Träger für Brennstoffzelle, Verfahren zu dessen Herstellung, Elektrode für Brennstoffzelle, Membran-Elektrodenanordnung für eine Brennstoffzelle und Brennstoffzellensystem

Dispositif de support destiné à une pile à combustible, procédé de préparation associé et électrode pour pile à combustible, ensemble membrane-électrode pour une pile à combustible et système de pile à combustible comprenant celui-ci

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Description

(a) Field of the Invention

[0001] The disclosure relates to a supporter for a fuel cell and a method of preparing the same, and an electrode, a membrane-electrode assembly, and a fuel cell system including the same.

(b) Description of the Related Art

[0002] A fuel cell is a power generation system for producing electrical energy through a chemical reaction of an oxidant and hydrogen from a hydrocarbon-based material such as methanol, ethanol, or natural gas. Such a fuel cell is a clean energy source with the potential to replace fossil fuels.

[0003] Fuel cells include a stack composed of unit cells, and produce various ranges of power. Since it has four to ten times higher energy density than a small lithium battery, it has been highlighted as a small portable power source.

[0004] Typical examples of fuel cells are polymer electrolyte membrane fuel cells (PEMFC) and direct oxidation fuel cells (DOFC). A direct oxidation fuel cell that uses methanol as a fuel is called a direct methanol fuel cell (DMFC). The polymer electrolyte fuel cell has an advantage of high energy density and high power, and a direct oxidation fuel cell has lower energy density than that of the polymer electrolyte fuel cell, but it has the advantages of easy handling of a fuel, being capable of operating at room temperature due to its low operation temperature, and no need for additional fuel reforming processors.

[0005] In the above-mentioned fuel cell system, the stack that generates electricity substantially includes several to scores of unit cells stacked adjacent to one another, and each unit cell is formed of a membrane-electrode assembly (MEA) and a separator (also referred to as a bipolar plate). The membrane-electrode assembly is composed of an anode (also referred to as a "fuel electrode" or an "oxidation electrode") and a cathode (also referred to as an "air electrode" or a "reduction electrode") that are separated by a polymer electrolyte membrane. A fuel is supplied to the anode and adsorbed on catalysts of the anode, and the fuel is oxidized to produce protons and electrons. The electrons are transferred into the cathode via an external circuit, and the protons are transferred into the cathode through the polymer electrolyte membrane. In addition, an oxidant is supplied to the cathode, and then the oxidant, protons, and electrons react on catalysts of the cathode to produce electricity along with water. EP1883131 discloses a supported catalyst for a fuel cell. JP2008-181696 discloses a catalyst for a fuel cell. US2011/151354 discloses an electrode catalyst for a fuel cell.

SUMMARY OF THE INVENTION

[0006] An embodiment of the present invention provides a supporter for a fuel cell exhibiting good stability as claimed in claim 1.

[0007] Another embodiment of the present invention provides a method of preparing the supporter for a fuel cell as claimed in claim 2.

[0008] Yet another embodiment of the present invention provides an electrode for a fuel cell including the supporter as claimed in claim 7.

[0009] Still another embodiment of the present invention provides a membrane-electrode assembly for a fuel cell including the electrode as claimed in claim 8. Still another embodiment of the present invention provides a fuel cell system including the membrane-electrode assembly as claimed in claim 9.

[0010] According to the present invention, a supporter for a fuel cell is provided that includes a carbonaceous material and a transition metal oxide coating layer formed on a surface of the carbonaceous material, wherein the surface of the carbonaceous material is covalently bonded with the transition metal oxide and the transition metal oxide has an average particle size of 1.5 nm to 10 nm.

[0011] The carbonaceous material comprises carbon nanotubes, optionally with at least one of graphite, denka black, ketjen black, acetylene black, carbon nanofiber, carbon nanowire, carbon nanoballs, and activated carbon.

[0012] The transition metal oxide is ZrO_2 . Optionally, this may be in combination with SnO_2 , WO_3 , TiO_2 , or InO_2 . In another embodiment, the transition metal oxide is a composite metal oxide including at least two of Zr, Sn, W, Ti, and In but with the proviso that it comprises ZrO_2 .

[0013] The amount of the transition metal oxide is preferably between 5 wt% to 95 wt% based on 100 wt% of the supporter.

[0014] Another embodiment of the present invention provides the supporter and an active metal supported on the supporter.

[0015] The active metal is preferably at least one selected from platinum, ruthenium, osmium, a platinum/ruthenium alloy, a platinum/osmium alloy, a platinum/palladium alloy, a platinum/M alloy (M is a transition element of Ga, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sn, Mo, W, Rh, Ru, or a combination thereof), or a combination thereof.

[0016] Another embodiment of the present invention provides a method of preparing the supporter for a fuel cell, including mixing a transition metal precursor and the carbonaceous material in the presence of a solvent. Still another embodiment provides an electrode for a fuel cell including an electrode substrate and a catalyst layer on the electrode substrate, and the catalyst layer includes the supporter.

[0017] Still another embodiment provides a membrane-electrode assembly for a fuel cell comprising the electrode as at least one of a cathode and an anode. For

example, the embodiment may relate to a membrane-electrode assembly including an anode and a cathode facing each other, and a polymer electrolyte membrane interposed between the cathode and the anode, wherein at least one of the cathode and the anode is the electrode.

[0018] According to a further embodiment of the present invention, provided is a fuel cell system that includes at least one electricity generating element including the membrane-electrode assembly and separators positioned at each side of the membrane-electrode assembly, a fuel supplier, and an oxidant supplier. The electricity generating element generates electrical energy through oxidation of a fuel and reduction of an oxidant. Furthermore, the fuel supplier supplies the fuel to the electricity generating element and the oxidant supplier supplies the oxidant to the electricity generating element. The supporter for a fuel cell according to one embodiment may provide a catalyst exhibiting good stability, activity, and cycle-life characteristics.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019]

FIG. 1 is a SEM photograph of the supporter for a fuel cell and a schematic view showing a supporter according to one embodiment.

FIG. 2 is a schematic view showing the structure of a fuel cell system according to one embodiment.

FIG. 3 is a graph showing X-ray diffraction results of the supporter according to Reference Example 1 and Examples 1 to 3.

FIG. 4 is a graph showing a size of ZrO_2 in the supporter according to Reference Example 1 and Examples 1 to 3.

FIG. 5 is a TEM photograph of the supporter according to Reference Example 1.

FIG. 6 is a TEM photograph of the supporter according to Example 1.

FIG. 7 is a TEM photograph of the supporter according to Example 2.

FIG. 8 is a TEM photograph of the supporter according to Example 3.

FIG. 9 is a 500,000-times enlarged TEM photograph of the catalyst according to Example 7.

FIG. 10A to FIG. 10D are 500,000-times enlarged SEM photographs according to Example 7.

FIG. 11 is a graph exhibiting activities of the catalysts according to Example 7 and Comparative Example 1.

FIG. 12 is a graph exhibiting activities of the catalysts according to Example 8 and Comparative Example 2.

FIG. 13 is a graph exhibiting activities of the catalysts according to Example 9 and Comparative Example 3.

FIG. 14 is a graph exhibiting an active surface area of the catalysts according to Example 7 and Com-

parative Example 1.

FIG. 15 is a SEM photograph of the catalyst according to Example 10 - Reference.

FIG. 16 is a SEM photograph of the catalyst according to Example 11 - Reference.

DETAILED DESCRIPTION OF THE INVENTION

[0020] One embodiment provides a supporter for a fuel cell that includes a carbonaceous material and a transition metal oxide coating layer on a surface of the supporter, wherein the transition metal oxide has an average particle size 1.5 nm to 10 nm. The carbonaceous material and the transitional metal oxide are covalently bonded.

[0021] FIG. 1 is a SEM photograph of the supporter for a fuel cell and a schematic view showing the structure of the supporter.

[0022] The carbonaceous material comprises carbon nanotubes with optionally at least one selected from graphite, denka black, ketjen black, acetylene black, carbon nanofiber, carbon nanowire, carbon nanoballs, and activated carbon.

[0023] The transition metal oxide comprises ZrO_2 , optionally in combination with SnO_2 , WO_3 , TiO_2 , or InO_2 , and optionally the composite metal oxide includes at least two selected from Zr, Sn, W, Ti, or In with the proviso that it comprises ZrO_2 . The transition metal oxide has an average size of 1.5 nm to 10 nm.

[0024] The amount of the transition metal oxide is 4 wt% to 96 wt% (e.g. 5 wt% to 95 wt%) based on 100 wt% of the total supporter, and in another embodiment, 30 wt% to 50 wt%. When the amount of the transition metal oxide falls in the above ranges, the supporter exhibits good stability and electrical conductivity.

[0025] The amount of transition metal oxide is optionally between 10 wt% to 90 wt%, 15 wt% to 85 wt%, such as 20 wt% to 70 wt%, (e.g. 25 wt% to 60 wt%).

[0026] The supporter according to one embodiment includes the coating layer including the carbonaceous material and metal oxide, so it has advantageous of high conductivity owing to the carbonaceous material and thermal/electrochemical stability owing to the metal oxide. In particular, since the carbonaceous material and the metal oxide are covalently bonded, it is advantageous for preventing separation of the metal oxide from the supporter while working for a long time.

[0027] Another embodiment provides a method of preparing the supporter, wherein the method comprises mixing a transition metal oxide precursor comprising a Zr-containing acetylacetonate, acetate, chloride, or a combination thereof and the carbonaceous material in the presence of a solvent selected from ethanol, water, isopropyl alcohol, or a combination thereof and the mixing ratio of the transition metal precursor and the carbonaceous material is controlled to obtain a mixing ratio of the transition metal oxide and the carbonaceous material that is 4:96 to 96:4 wt% and the mixing step is performed at 90 °C to 200 °C. The carbonaceous material is optionally

one oxidized by acids. The acid used is optionally selected from nitric acid, sulfuric acid, or a combination thereof.

[0028] The oxidization includes mixing/refluxing the carbonaceous material and the acid and washing/drying. The acid used has a concentration of 0.1 M to 3 M.

[0029] According to this process, a "-OH" or "-O" functional group is presented on a surface of the carbonaceous material.

[0030] The transition metal precursor is a transition metal-included acetylacetonate, acetate, chloride, or a combination thereof. The transition metal comprises Zr, optionally in combination with Sn, W, Ti, or In.

[0031] The carbonaceous material comprises carbon nanotubes (optionally single-wall carbon nanotubes or multi-wall carbon nanotubes), optionally with at least one selected from graphite, denka black, ketjen black, acetylene black, carbon nanofiber, carbon nanowire, carbon nanoballs, or activated carbon. Suitably, the carbonaceous material comprises carbon nanotubes in combination with carbon nanofiber or carbon nanowire.

[0032] A mixing ratio of the transition metal precursor and the carbonaceous material is preferably from 5:95 to 95:5 wt%. In another embodiment, the mixing ratio of the transition metal precursor and the carbonaceous material is from 30:70 to 50:50 wt%. When the mixing ratio of the transition metal precursor and the carbonaceous material is out of the above range, i.e., the amount of the transition metal precursor decreases, sufficient durability cannot be obtained. Furthermore, as the amount of the transition metal precursor increases, the electrical conductivity may be reduced.

[0033] The mixing ratio is performed at 90°C to 200°C. The mixing ratio at the above temperature allows rapid synthesis and termination reaction, thereby reducing the particle size.

[0034] According to the above procedure, the transition metal precursor is adhered to a surface of the carbonaceous material and converted into a transition metal alkoxide. Particularly, if the carbonaceous material oxidized with acid is used, the transition metal precursor reacts with the "-OH" or "-O" functional group on the surface of the carbonaceous material to adhere to the surface of the carbonaceous material, thereby converting the transition metal alkoxide.

[0035] Another embodiment provides a catalyst for a fuel cell including the supporter and an active metal supported on the supporter.

[0036] The active metal is preferably at least one selected from platinum, ruthenium, osmium, a platinum/ruthenium alloy, a platinum/osmium alloy, a platinum/palladium alloy, a platinum/M alloy (M is a transition element of Ga, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sn, Mo, W, Rh, Ru, or a combination thereof), or a combination thereof. The catalyst according to another embodiment is used for an anode and/or a cathode. The catalyst can be the same regardless of whether it is used in the anode or the cathode. However, a direct oxidation fuel cell optionally includes a platinum-ruthenium alloy as the active metal

as an anode catalyst in order to prevent catalyst poisoning due to CO generated during the anode reaction. Specific examples of the catalyst include Pt, Pt/Ru, Pt/W, Pt/Ni, Pt/Sn, Pt/Mo, Pt/Pd, Pt/Fe, Pt/Cr, Pt/Co, Pt/Ru/W, Pt/Ru/Mo, Pt/Ru/V, Pt/Fe/Co, Pt/Ru/Rh/Ni, Pt/Ru/Sn/W, and a combination thereof, but are not limited thereto.

[0037] The method of supporting the active metal on the supporter is well-known in the related field, and a detailed description thereof is omitted.

[0038] Another embodiment provides an electrode for a fuel cell including a catalyst layer including the catalyst and an electrode substrate.

[0039] The catalyst layer optionally further includes a binder resin to improve its adherence and proton transfer properties.

[0040] The binder resin (referred as "ionomer") is optionally a proton conductive polymer resin having a cation exchange group selected from the group consisting of a sulfonic acid group, a carboxylic acid group, a phosphoric acid group, a phosphonic acid group, and derivatives thereof at its side chain.

[0041] Examples of the polymer include at least one proton conductive polymer selected from the group consisting of a fluorine-based polymer, a benzimidazole-based polymer, a polyimide-based polymer, a polyetherimide-based polymer, a polyphenylenesulfide-based polymer, a polysulfone-based polymer, a polyethersulfone-based polymer, a polyetherketone-based polymer, a polyether-etherketone-based polymer, or a polyphenylquinoxaline-based polymer.

[0042] In one embodiment, the proton conductive polymer is at least one selected from the group consisting of poly(perfluorosulfonic acid), poly(perfluorocarboxylic acid), a sulfonic acid-containing copolymer of tetrafluoroethylene and fluorovinylether, polyetherketone sulfide, an aryl ketone, poly(2,2'-m-phenylene)-5,5'-bibenzimidazole, and poly(2,5-benzimidazole).

[0043] The hydrogen (H) in the cation exchange group of the proton conductive polymer is optionally substituted with Na, K, Li, Cs, or tetrabutylammonium. When the H in the cation exchange group of the terminal end of the proton conductive polymer side chain is substituted with Na or tetrabutylammonium, NaOH or tetrabutylammonium hydroxide is optionally used during preparation of the catalyst composition, respectively. When the H is substituted with K, Li, or Cs, a suitable compound for the substitution is used. Since such a substitution is known in this art, a detailed description thereof is omitted.

[0044] The binder resins are used singularly or in combination. They are optionally used along with non-conductive polymers to improve adherence with a polymer electrolyte membrane. The binder resins are used in a controlled amount to adapt to their purposes.

[0045] Examples of the non-conductive polymers include at least one selected from the group consisting of polytetrafluoroethylene (PTFE), a tetrafluoroethylene-hexafluoropropylene copolymer (FEP), a tetrafluoroethylene-perfluoroalkylvinylether copolymer (PFA), an eth-

ylene/tetrafluoroethylene copolymer (ETFE), an ethylenechlorotrifluoro-ethylene copolymer (ECTFE), polyvinylidenefluoride, a copolymer of polyvinylidenefluoride-hexafluoropropylene (PVdF-HFP), dodecylbenzenesulfonic acid, and sorbitol.

[0046] The electrode substrates support the anode and cathode and provide a path for transferring the fuel and oxidant to catalyst layers. In one embodiment, the electrode substrates are formed from a material such as carbon paper, carbon cloth, carbon felt, or a metal cloth (a porous film composed of metal fiber or a metal film disposed on a surface of a cloth composed of polymer fibers). The electrode substrate is not limited thereto.

[0047] The electrode substrates may be treated with a fluorine-based resin to be water-repellent to prevent deterioration of reactant diffusion efficiency due to water generated during operation of a fuel cell.

[0048] Examples of the fluorine-based resin include polytetrafluoroethylene, polyvinylidene fluoride, polyhexafluoropropylene, polyperfluoroalkylvinylether, polyperfluorosulfonylfluoride, alkoxyvinyl ether, fluorinated ethylene propylene, polychlorotrifluoroethylene, and copolymers thereof. The electrode for a fuel cell optionally further includes a microporous layer to increase reactant diffusion effects of the electrode substrate. The microporous layer generally includes conductive powders with a particular particle diameter, for example carbon powder, carbon black, acetylene black, activated carbon, carbon fiber, fullerene, carbon nanotubes, carbon nanowire, carbon nanohorns, or carbon nanorings. The microporous layer is formed by coating a composition including a conductive powder, a binder resin, and a solvent on the electrode substrate.

[0049] The binder resin optionally includes polytetrafluoroethylene, polyvinylidenefluoride, polyhexafluoropropylene, polyperfluoroalkylvinylether, polyperfluorosulfonylfluoride, alkoxyvinyl ether, polyvinylalcohol, celluloseacetate, a copolymer thereof, and the like. The binder resin may optionally include polytetrafluoroethylene, polyvinylidenefluoride, polyhexafluoropropylene, polyperfluoroalkylvinylether, polyperfluorosulfonylfluoride, alkoxyvinyl ether, polyvinylalcohol, celluloseacetate, a copolymer thereof, and the like.

[0050] The coating method used can be selected from, but is not limited to, screen printing, spray coating, doctor blade methods, gravure coating, dip coating, silk screening, painting, and so on, depending on the viscosity of the composition.

[0051] According to another embodiment, a membrane-electrode assembly for a fuel cell including the electrode as at least one of a cathode and an anode is provided.

[0052] The membrane-electrode assembly includes an anode and a cathode facing each other, and a polymer electrolyte membrane disposed between the anode and cathode. The polymer electrolyte membrane may include any kind generally used for a fuel cell, formed of a polymer resin, and having proton conductivity, without any partic-

ular limit.

[0053] Examples thereof include a polymer resin having a cation exchange group selected from a sulfonic acid group, a carboxylic acid group, a phosphoric acid group, a phosphonic acid group, and derivatives thereof, at the side chain. Examples of the polymer resin may include at least one selected from a fluorine-based polymer, a benzimidazole-based polymer, a polyimide-based polymer, a polyetherimide-based polymer, a polyphenylenesulfide-based polymer, a polysulfone-based polymer, a polyethersulfone-based polymer, a polyetherketone-based polymer, a polyether-etherketone-based polymer, and a polyphenylquinoxaline-based polymer.

[0054] Preferred examples include poly(perfluorosulfonic acid) (generally, commercially available as Nafion), poly(perfluorocarboxylic acid), a copolymer of tetrafluoroethylene having a sulfonic acid group and fluorovinylether, defluorinated polyetherketone sulfide, aryl ketone, poly(2,2'-(m-phenylene)-5,5'-bibenzimidazole, poly(2,5-benzimidazole), and the like.

[0055] The hydrogen (H) is substituted with Na, K, Li, Cs, or tetrabutylammonium in a proton conductive group of the proton conductive polymer. When the hydrogen (H) is substituted with Na in an ion exchange group at the terminal end of the proton conductive group, NaOH is used. When the hydrogen (H) is substituted with tetrabutylammonium, tributylammonium hydroxide is used. K, Li, or Cs can also be substituted with use of appropriate compounds.

[0056] A method of substituting hydrogen (H) is known in the related art, and therefore is not further described in detail. In addition, the proton conductive polymer including substituted Na, K, Li, Cs, or tetrabutylammonium is converted into a proton type during the acid treatment of a catalyst layer.

[0057] According to another embodiment, a fuel cell system including at least one electricity generating element, a fuel supplier, and an oxidant supplier is provided. The electricity generating element includes the membrane-electrode assembly according to one embodiment and a separator (referred to as a "bipolar plate"). The electricity generating element generates electrical energy through oxidation of a fuel and reduction of an oxidant.

[0058] Furthermore, the fuel supplier supplies the fuel to the electricity generating element and the oxidant supplier supplies the oxidant such as air or oxygen to the electricity generating element. In one embodiment, the fuel includes hydrogen or a hydrocarbon fuel in the form of a gas or liquid. Examples thereof include methanol, ethanol, propanol, butanol, natural gas, and the like.

[0059] The schematic structure of a fuel cell system according to one embodiment is shown in FIG. 2, which will be described in detail with reference to this accompanying drawing as follows. FIG. 2 shows a fuel cell system supplying a fuel and an oxidant to an electricity generating element using a pump, but the fuel cell system according to the embodiment is not limited to such structures.

[0060] The fuel cell system of the embodiment alternately includes a structure wherein a fuel and an oxidant are provided in a diffusion manner without a pump. The fuel system 1 includes at least one electricity generating element 3 that generates electrical energy by oxidation of a fuel and reduction of an oxidant, a fuel supplier 5 for supplying the fuel, and an oxidant supplier 7 for supplying an oxidant to the electricity generating element 3.

[0061] In addition, the fuel supplier 5 is equipped with a tank 9, which stores fuel, and a fuel pump 11, which is connected therewith. The fuel pump 11 supplies fuel that is stored in the tank 9 with a predetermined pumping power. The oxidant supplier 7, which supplies the electricity generating element 3 with an oxidant, is equipped with at least one oxidant pump 13 for supplying an oxidant with a predetermined pumping power.

[0062] The electricity generating element 3 includes a membrane-electrode assembly 17, which oxidizes hydrogen or a fuel and reduces an oxidant, and separators 19 and 19' that are respectively positioned at opposite sides of the membrane-electrode assembly and that supply hydrogen or a fuel, and an oxidant, respectively.

[0063] A stack 15 is provided by stacking at least one electricity generating element 3.

[0064] The following examples illustrate the present invention in more detail. However, it is understood that the disclosure is not limited by these examples.

(Reference Example 1)

[0065] Zirconium (IV) acetylacetonate and carbon black (CB-1) were mixed under an ethanol reducing agent at 200 °C to produce a reaction. At this time, the mixing ratio of zirconium (IV) acetylacetonate and multi-wall carbon nanotubes was 12 wt%:88 wt%. The ethanol reduction provided a supporter with a zirconium oxide-included coating layer on a surface of the multi-wall carbon nanotubes, and the multi-wall carbon nanotubes and zirconium oxide were covalently bonded.

(Example 1)

[0066] A supporter for a fuel cell was prepared by the same procedure as in Reference Example 1, except that the mixing ratio of zirconium (IV) acetylacetonate and carbon black (CB-1) was 35 wt%:65 wt%.

(Example 2)

[0067] A supporter for a fuel cell was prepared by the same procedure as in Reference Example 1, except that the mixing ratio of zirconium (IV) acetylacetonate and carbon black (CB-1) was 50 wt%:50 wt%.

(Example 3)

[0068] A supporter for a fuel cell was prepared by the same procedure as in Reference Example 1, except that

the mixing ratio of zirconium (IV) acetylacetonate and carbon black (CB-1) was 70 wt%:30 wt%.

(Example 4)

[0069] A supporter for a fuel cell was prepared by the same procedure as in Reference Example 1, except that the mixing ratio of zirconium (IV) acetylacetonate and carbon black (CB-1) was 80 wt%:20 wt%.

(Example 5)

[0070] A supporter for a fuel cell was prepared by the same procedure as in Reference Example 1, except that crystalline carbon black (CB-500) which was prepared by heat-treating carbon black (CB-1) at 2000 °C was used instead of carbon black (CB-1).

(Example 6)

[0071] A supporter for a fuel cell was prepared by the same procedure as in Reference Example 1, except that crystalline carbon black (CB-1000) which was prepared by heat-treating carbon black (CB-1) at 2500 °C was used instead of carbon black (CB-1).

* Determination of X-ray diffraction (XRD)

[0072] The X-ray diffraction for the supporters according to Reference Example 1 and Examples 1 to 3 was measured using CuK α radiation. The results are shown in FIG. 3. As shown in FIG. 3, as the amount of zirconium (IV) acetylacetonate increases, the intensity of the peaks of t-ZrO₂ (200) and t-ZrO₂ (111) increases. It can be known from the result that the tetragonal structure is uniformly formed.

* Measurements for zirconium oxide particle size

[0073] The size of ZrO₂ in the supporter according Reference Example 1 and Examples 1 to 3 was measured. The results are shown in FIG. 4. As shown in FIG. 4, as the amount of zirconium (IV) acetylacetonate, i.e., the amount of ZrO₂ in the supporter increases, the particle size increases. In FIG. 4, the amount of ZrO₂ shown is based upon the weight percentage of zirconium (IV) acetylacetonate used to manufacture the supporter.

* TEM photograph

[0074] TEM photographs (400,000-times enlarged) of the supporter according to Reference Example 1 and Examples 1 to 3 are shown in FIGS. 5 to 8, respectively. It can be known from FIGS. 5 to 8 that the bright portions are wider as the amount of zirconium (IV) acetylacetonate is increased. The bright portions in FIGS. 5 to 8 indicate zirconium oxide so that as the amount of zirconium (IV) acetylacetonate increases, the dispersion abil-

ity improves.

(Example 7)

[0075] Pt was supported on the supporter according to Example 4 by a polyol method to prepare a Pt/Zr-carbon black catalyst (Pt/Zr-CB-1).

(Example 8)

[0076] A catalyst (Pt/Zr-CB-500) was prepared by the same procedure as in Example 7, except that the supporter according to Example 5 was used.

(Example 9)

[0077] A catalyst (Pt/Zr-CB-1000) was prepared by the same procedure as in Example 7, except that the supporter according to Example 6 was used.

(Comparative Example 1)

[0078] Pt was supported on a carbon black (CB-1) by a polyol method to prepare a catalyst (Pt/CB-1).

(Comparative Example 2)

[0079] Pt was supported on crystalline carbon black (CB-500) which was prepared by heat-treating the carbon black (CB-1) at 2000°C, by a polyol method, to prepare a catalyst (Pt/CB-500).

(Comparative Example 3)

[0080] Pt was supported on crystalline carbon black (CB-1000) which was prepared by heat-treating the carbon black (CB-1) at 2500°C, by a polyol method, to prepare a catalyst (Pt/CB-1000).

* TEM photograph

[0081] 500,000-times enlarged TEM photographs of the catalyst according to Example 7 are shown in FIG. 9 and FIGS. 10A to 10D. The TEM photographs in FIG. 9 and FIGS. 10A to 10D were obtained from various surfaces of the catalyst according to Example 7. They indicate that Pt and ZrO₂ are uniformly distributed in the total catalyst.

* Measurements of the catalyst activity

[0082] The catalyst activity of the catalyst according to Examples 7 to 9 and Comparative Examples 1 to 3 was measured. The results according to Example 7 and Comparative Example 1 are shown in FIG. 11, the results according to Example 8 and Comparative Example 2 are shown in FIG. 12, and the results according to Example 9 and Comparative Example 3 are shown in FIG. 13.

[0083] The catalyst activity was obtained by a CV (cyclic voltammetry) experiment. At this time, a saturated calomel electrode (SCE) was used as a standard electrode. Furthermore, the working electrode obtained by mixing 50 wt% of the catalyst and 50 wt% of an ionomer in an isopropyl alcohol solvent to prepare a catalyst ink slurry and coating the ink slurry on a glassy carbon rod was used. As a counter electrode, a Pt mesh was used. The CV experiment was performed in an aqueous solution of 0.1 M HClO₄ and measured at a scan rate of 10 mV/second.

[0084] The results from FIGS. 11 to 13 indicated that the catalyst activity according to Examples 7 to 9 is excellent, compared to Examples 1 to 3, since the graph area of the catalyst according to Examples 7 to 9 is wider than that according to Comparative Examples 1 to 3.

* Measurements of activated surface areas of catalyst

[0085] The activated surface areas of catalysts according to Example 7 and Comparative Example 1 were measured by an electrochemical experiment. The activated surface area percentages (%) after 1000 cycles were calculated based on 100 % of the activated surface area of the catalyst.

[0086] The results are shown in FIG. 14. From FIG. 14, it can be seen that the deterioration ratio of the catalyst according to Example 7 is higher than that according to Comparative Example 7. Thus, the catalyst according to Example 7 maintains activity for a long time, compared to Comparative Example 1.

(Example 10 - Reference)

[0087] A supporter for a fuel cell was prepared by the same procedure as in Reference Example 1, except that Sn acetylacetonate was used instead of zirconium (IV) acetylacetonate, and the mixing ratio of Sn acetylacetonate and carbon black (CB-1) was 30 wt%:70 wt%.

[0088] Pt was supported on the supporter by the same procedure as in Example 7 to prepare a catalyst.

(Example 11 - Reference)

[0089] A supporter for a fuel cell was prepared by the same procedure as in Reference Example 1, except that W chloride was used instead of zirconium (IV) acetylacetonate, and the mixing ratio of W chloride and carbon black (CB-1) was 10 wt%:90 wt%.

[0090] Pt was supported on the supporter by the same procedure as in Example 7 to prepare a catalyst.

* TEM photograph

[0091] A TEM photograph of the catalyst according to Example 10 is shown in FIG. 15. As shown in FIG. 15, Pt and Sn were uniformly distributed in the total catalyst.

[0092] Furthermore, FIG. 16 is a TEM photograph of

the catalyst according to Example 11. As shown in FIG. 16, Pt and W were uniformly distributed in the total catalyst.

[0093] While this invention has been described in connection with what is presently considered to be practical embodiments, it is to be understood that the invention is not limited to the disclosed embodiments, but, on the contrary, is intended to cover various modifications and equivalent arrangements included within the scope of the appended claims.

Claims

1. A supporter for use in a fuel cell catalyst, comprising:

a carbonaceous material comprising carbon nanotubes; and
a transition metal oxide coating layer on a surface of the carbonaceous material wherein the transition metal oxide comprises ZrO_2 , wherein said surface of the carbonaceous material is covalently bonded to the transition metal oxide, wherein the transition metal oxide has an average particle size 1.5 nm to 10 nm, wherein the supporter is prepared by a process including mixing a transition metal oxide precursor comprising a Zr-containing acetylacetonate, acetate, chloride, or a combination thereof and the carbonaceous material in the presence of a solvent selected from ethanol, water, isopropyl alcohol, or a combination thereof and the ratio of the transition metal oxide and the carbonaceous material that is 4:96 to 96:4 wt% and the mixing step is performed at 90 °C to 200 °C.

2. A method of preparing the supporter for a fuel cell catalyst as claimed in claim 1, wherein the method comprises mixing a transition metal oxide precursor comprising a Zr-containing acetylacetonate, acetate, chloride, or a combination thereof and the carbonaceous material in the presence of a solvent selected from ethanol, water, isopropyl alcohol, or a combination thereof and the mixing ratio of the transition metal precursor and the carbonaceous material is controlled to obtain a mixing ratio of the transition metal oxide and the carbonaceous material that is 4:96 to 96:4 wt% and the mixing step is performed at 90 °C to 200 °C..

3. The method of claim 2, wherein the carbonaceous material is subjected to an oxidation step with an acid before mixing with the transition metal precursor, optionally wherein:

- (a) the acid is nitric acid, sulfuric acid, or a combination thereof; and/or
- (b) the oxidation step comprises mixing/reflux-

ing the carbonaceous material with the acid and washing/drying the resulting product; and/or
(c) the acid has a concentration of 0.1 M to 3 M.

4. The method of any one of Claims 2 to 3, wherein the carbonaceous material is at least one selected from single-wall carbon nanotubes or multi-wall carbon nanotubes.

5. The method of any one of Claims 2 to 4 further comprising supporting an active metal on the supporter comprising the carbonaceous material and the transition metal oxide.

6. A catalyst for a fuel cell comprising the supporter of Claim 1, wherein an active metal is supported on the supporter, optionally wherein the selected active metal may be at least one selected from platinum, ruthenium, osmium, a platinum/ruthenium alloy, a platinum/osmium alloy, a platinum/palladium alloy, a platinum/M alloy (M is a transition element of Ga, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sn, Mo, W, Rh, Ru, or a combination thereof), or a combination thereof.

7. An electrode for a fuel cell comprising an electrode substrate and a catalyst layer on said electrode substrate, wherein said catalyst layer comprises a catalyst according to Claim 6.

8. A membrane-electrode assembly for a fuel cell comprising the electrode of Claim 7 as at least one of a cathode and an anode, optionally wherein the membrane-electrode assembly includes an anode and a cathode facing each other, and a polymer electrolyte membrane disposed between the anode and cathode.

9. A fuel cell system comprising at least one electricity generating element, a fuel supplier, and an oxidant supplier, wherein the electricity generating element comprises the membrane-electrode assembly according to Claim 8 and a separator.

Patentansprüche

1. Träger zur Verwendung in einem Brennstoffzellenkatalysator, der Folgendes umfasst:

ein kohlenstoffhaltiges Material, das Kohlenstoff-Nanoröhrchen umfasst; und
eine Überzugsschicht eines Übergangsmetalloxids auf einer Oberfläche des kohlenstoffhaltigen Materials, wobei das Übergangsmetalloxid ZrO_2 umfasst, wobei die Oberfläche des kohlenstoffhaltigen Materials kovalent an das Übergangsmetalloxid gebunden ist, wobei das Übergangsmetalloxid eine mittlere Teilchengröße

- von 1,5 nm bis 10 nm aufweist, wobei der Träger hergestellt wird durch ein Verfahren, welches das Mischen eines Übergangsmetalloxidvorläufers, der ein Zr-haltiges Acetylacetonat, Acetat, Chlorid oder eine Kombination davon umfasst und des kohlenstoffhaltigen Materials in Gegenwart eines Lösemittels umfasst, das ausgewählt wird aus Ethanol, Wasser, Isopropylalkohol oder einer Kombination davon, und das Verhältnis des Übergangsmetalloxids und des kohlenstoffhaltigen Materials 4:96 bis 96:4 Gew.-% beträgt, und der Mischschritt bei 90 °C bis 200 °C durchgeführt wird.
2. Verfahren zur Herstellung des Trägers für einen Brennstoffzellenkatalysator wie in Anspruch 1 beansprucht, wobei das Verfahren das Mischen eines Übergangsmetalloxidvorläufers, der ein Zr-haltiges Acetylacetonat, Acetat, Chlorid oder eine Kombination davon umfasst und des kohlenstoffhaltigen Materials in Gegenwart eines Lösemittels umfasst, welches ausgewählt wird aus Ethanol, Wasser, Isopropylalkohol, oder einer Kombination davon, und das Mischungsverhältnis des Übergangsmetallvorläufers und des kohlenstoffhaltigen Materials gesteuert wird, um ein Mischungsverhältnis des Übergangsmetalloxids und des kohlenstoffhaltigen Materials zu erhalten, das 4:96 bis 96:4 Gew.-% beträgt, und der Mischschritt bei 90 °C bis 200 °C durchgeführt wird.
 3. Verfahren nach Anspruch 2, wobei das kohlenstoffhaltige Material einem Oxidationsschritt mit einer Säure vor dem Mischen mit dem Übergangsmetallvorläufer unterworfen wird, wobei wahlweise:
 - (a) die Säure Salpetersäure, Schwefelsäure oder eine Kombination davon ist; und/oder
 - (b) der Oxidationsschritt das Mischen/den Rückfluss des kohlenstoffhaltigen Materials mit der Säure und das Waschen/Trocknen des resultierenden Produkts umfasst; und/oder
 - (c) die Säure eine Konzentration von 0,1 M bis 3 M aufweist.
 4. Verfahren nach einem der Ansprüche 2 bis 3, wobei das kohlenstoffhaltige Material mindestens eines ist, das ausgewählt wird aus einwandigen Kohlenstoff-Nanoröhrchen oder mehrwandigen Kohlenstoff-Nanoröhrchen.
 5. Verfahren nach einem der Ansprüche 2 bis 4, das ferner das Tragen eines aktiven Metalls auf dem Träger umfasst, der das kohlenstoffhaltige Material und das Übergangsmetalloxid umfasst.
 6. Katalysator für eine Brennstoffzelle, der den Träger nach Anspruch 1 umfasst, wobei ein aktives Metall von dem Träger getragen wird, wobei das ausge-
- wählte aktive Metall wahlweise eines sein kann, das ausgewählt ist aus Platin, Ruthenium, Osmium, einer Platin/Ruthenium-Legierung, einer Platin/Osmium-Legierung, einer Platin/Palladium-Legierung, einer Platin/M-Legierung (M ist ein Übergangselement aus Ga, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sn, Mo, W, Rh, Ru oder eine Kombination davon) oder einer Kombination davon.
7. Elektrode für eine Brennstoffzelle mit einem Elektrodenträger und einer Katalysatorschicht auf dem Elektrodenträger, wobei die Katalysatorschicht einen Katalysator nach Anspruch 6 umfasst.
 8. Membran-Elektroden-Anordnung für eine Brennstoffzelle, welche die Elektrode nach Anspruch 7 als mindestens eine Kathode und/oder eine Anode umfasst, wobei die Membran-Elektroden-Anordnung wahlweise eine Anode und eine Kathode umfasst, die einander zugewandt sind, und eine Polymerelektrolyt-Membran, die zwischen der Anode und der Kathode angeordnet sind.
 9. Brennstoffzellensystem mit mindestens einem Elektrizitätserzeugungselement, einem Brennstofflieferanten und einem Oxidationsmittellieferanten, wobei das Elektrizitätserzeugungselement die Membranelektrodenanordnung nach Anspruch 8 und einen Separator umfasst.

Revendications

1. Support destiné à être utilisé dans un catalyseur de pile à combustible, comprenant :

un matériau carboné comprenant des nanotubes de carbone ; et
 une couche de revêtement d'oxyde de métal de transition sur une surface du matériau carboné où l'oxyde de métal de transition comprend du ZrO_2 , où ladite surface du matériau carboné est liée de manière covalente à l'oxyde de métal de transition, où l'oxyde de métal de transition a une taille moyenne de particule allant de 1,5 nm à 10 nm, où le support est préparé par un procédé comportant le mélange d'un précurseur d'oxyde de métal de transition comprenant un acétylacétonate, un acétate, un chlorure contenant du Zr ou une combinaison de ceux-ci et le matériau carboné en présence d'un solvant choisi entre l'éthanol, l'eau, l'alcool isopropylique ou une combinaison de ceux-ci et le rapport entre l'oxyde de métal de transition et le matériau carboné est compris entre 4:96 et 96:4% en poids et l'étape de mélange est effectuée à une température comprise entre 90°C et 200°C.

2. Procédé de préparation du support pour un catalyseur de pile à combustible tel que revendiqué dans la revendication 1, dans lequel le procédé comprend le mélange d'un précurseur d'oxyde de métal de transition comprenant un acétylacétonate, un acétate, un chlorure contenant du Zr ou une combinaison de ceux-ci et le matériau carboné en présence d'un solvant choisi entre l'éthanol, l'eau, l'alcool isopropylique ou une combinaison de ceux-ci et le rapport de mélange du précurseur de métal de transition et du matériau carboné est régulé pour obtenir un rapport de mélange entre l'oxyde de métal de transition et le matériau carboné qui est compris entre 4:96 et 96:4% en poids et l'étape de mélange est effectuée à une température comprise entre 90°C et 200°C. 5
3. Procédé de la revendication 2, dans lequel le matériau carboné est soumis à une étape d'oxydation avec un acide avant le mélange avec le précurseur de métal de transition, facultativement dans lequel : 10
 - (a) l'acide est l'acide nitrique, l'acide sulfurique ou une combinaison de ceux-ci ; et/ou
 - (b) l'étape d'oxydation comprend le mélange/reflux du matériau carboné avec l'acide et le lavage/séchage du produit résultant ; et/ou
 - (c) l'acide a une concentration allant de 0,1 M à 3 M. 20
4. Procédé de l'une quelconque des revendications 2 et 3, dans lequel le matériau carboné est au moins un élément choisi entre des nanotubes de carbone monoparoi et des nanotubes de carbone multiparoi. 25
5. Procédé de l'une quelconque des revendications 2 à 4, comprenant en outre le fait de supporter un métal actif sur le support comprenant le matériau carboné et l'oxyde de métal de transition. 30
6. Catalyseur pour une pile à combustible comprenant le support de la revendication 1, dans lequel un métal actif est supporté sur le support, facultativement dans lequel le métal actif choisi peut être au moins un élément choisi entre le platine, le ruthénium, l'osmium, un alliage platine/ruthénium, un alliage platine/osmium, un alliage platine/palladium, un alliage platine/M (M est un élément de transition Ga, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sn, MO, W, Rh, Ru ou une combinaison de ceux-ci) ou une combinaison de ceux-ci. 35
7. Électrode pour une pile à combustible comprenant un substrat d'électrode et une couche de catalyseur sur ledit substrat d'électrode, où ladite couche de catalyseur comprend un catalyseur selon la revendication 6. 40
8. Ensemble membrane-électrodes pour une pile à combustible comprenant l'électrode de la revendication 7 comme au moins l'une d'une cathode et d'une anode, facultativement où l'ensemble membrane-électrodes comporte une anode et une cathode se faisant face, et une membrane électrolytique polymère disposée entre l'anode et la cathode. 45
9. Système de pile à combustible comprenant au moins un élément de production d'électricité, un dispositif d'alimentation en carburant et un dispositif d'alimentation en oxydant, où l'élément de production d'électricité comprend l'ensemble membrane-électrodes selon la revendication 8 et un séparateur. 50

FIG. 1

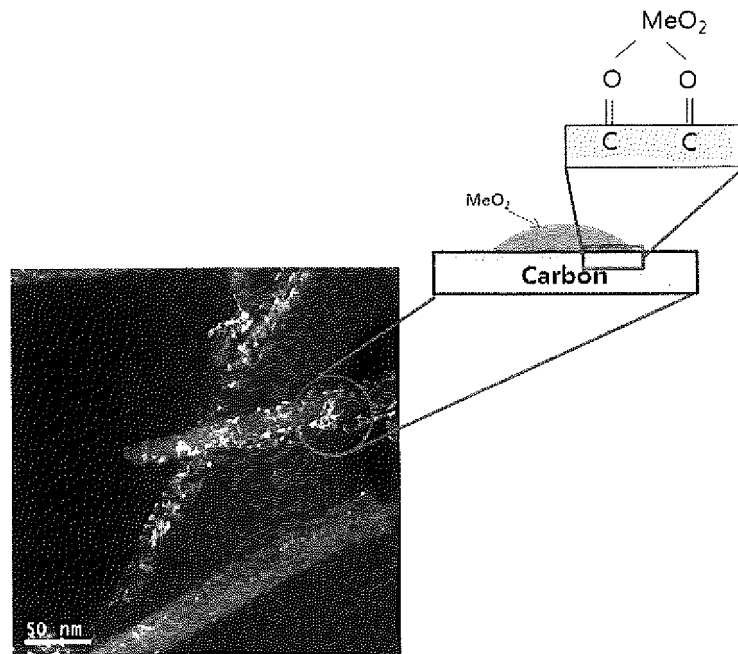


FIG. 2

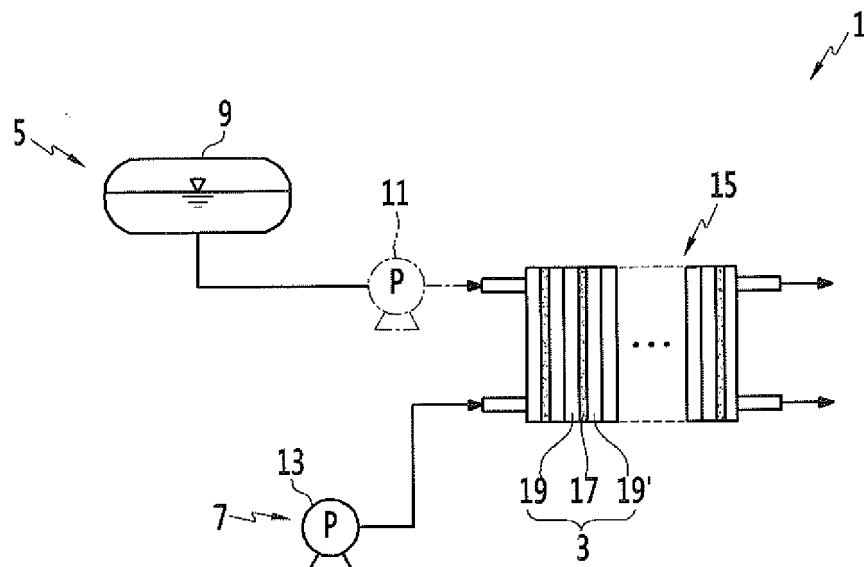


FIG.3

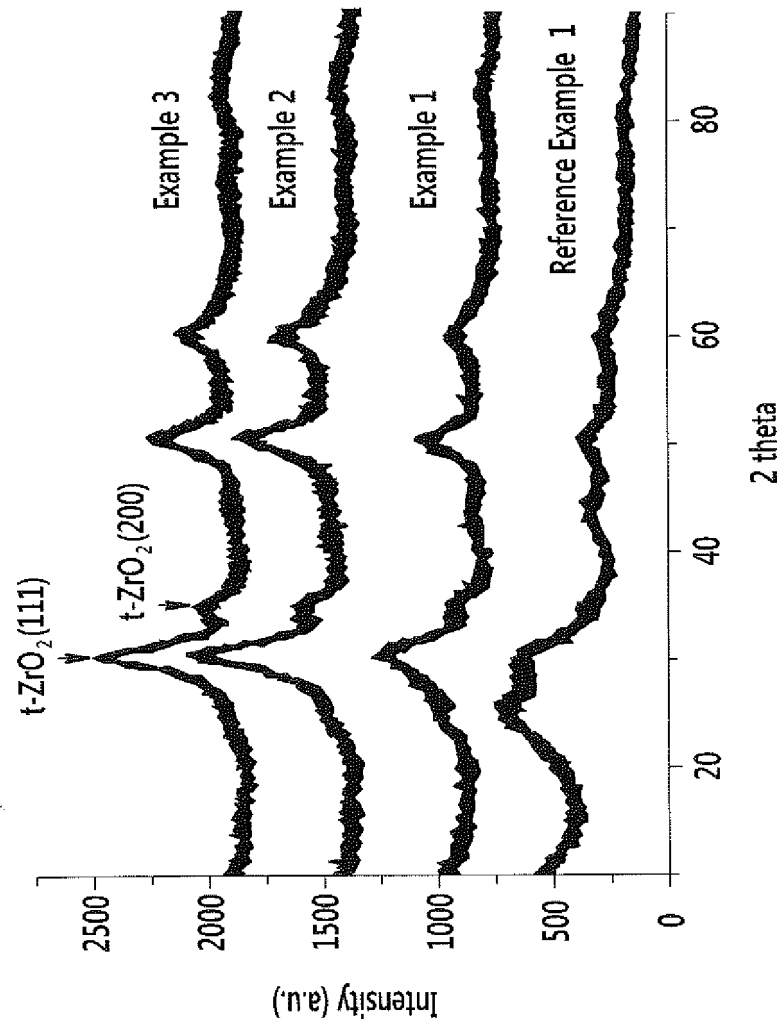


FIG.4

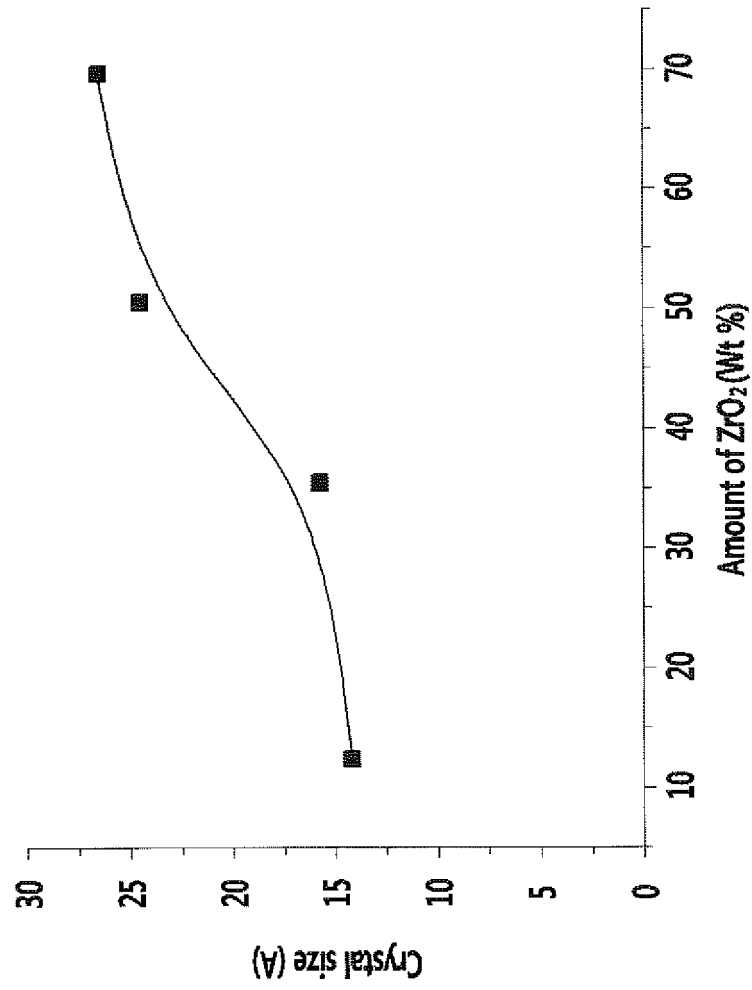


FIG. 5

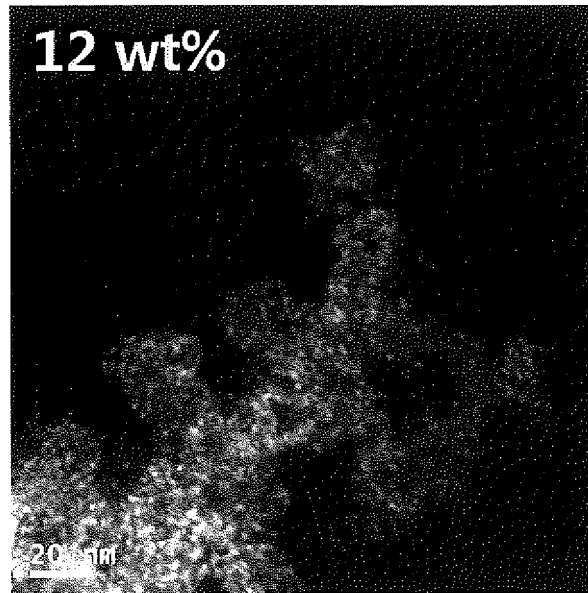


FIG. 6

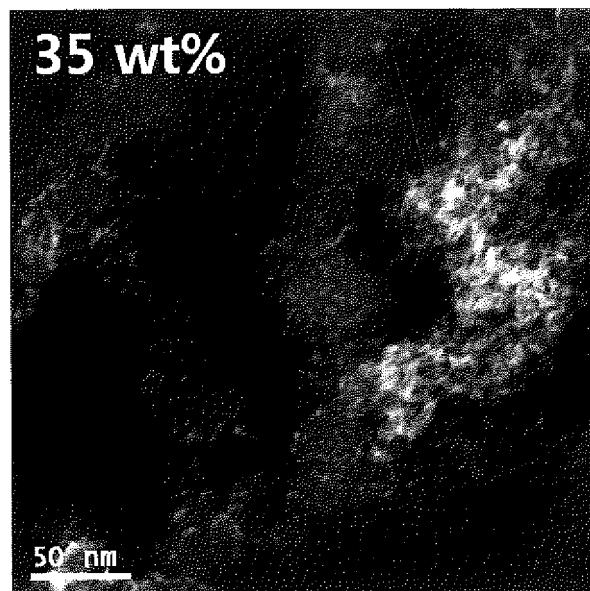


FIG. 7

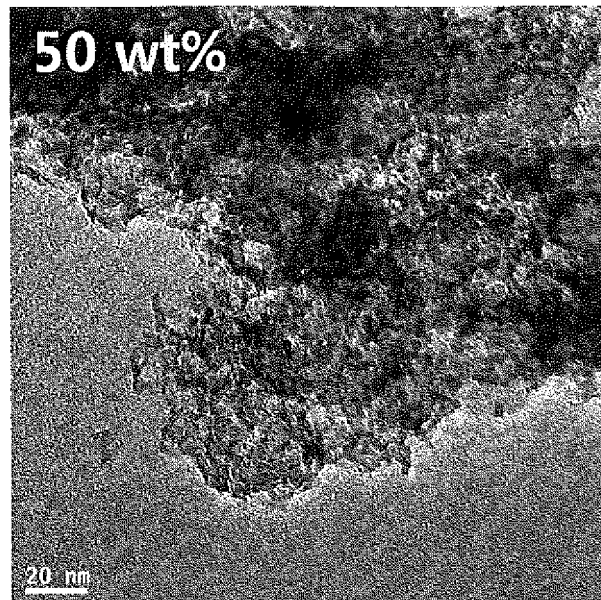


FIG. 8

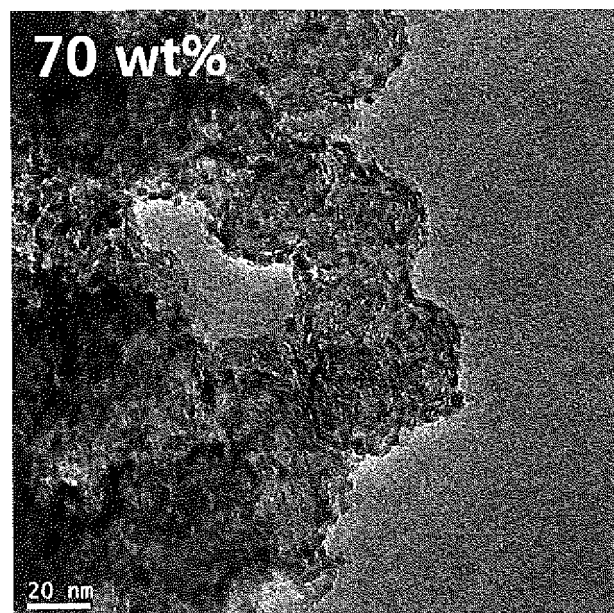


FIG. 9

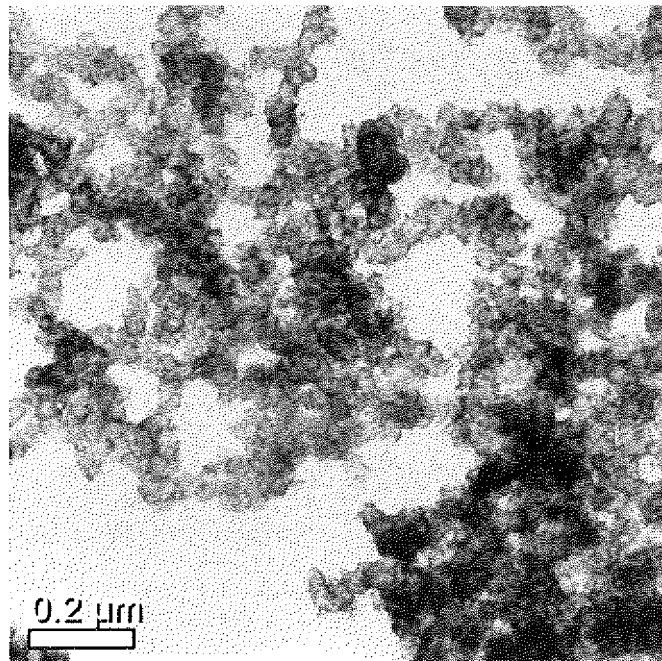


FIG. 10A

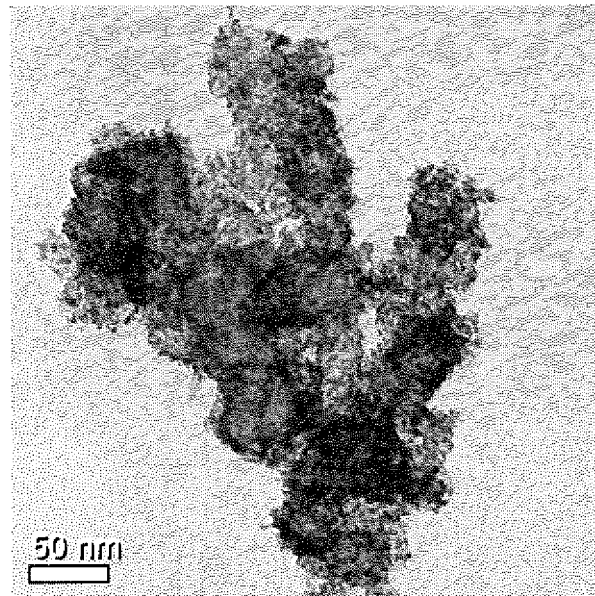


FIG. 10B

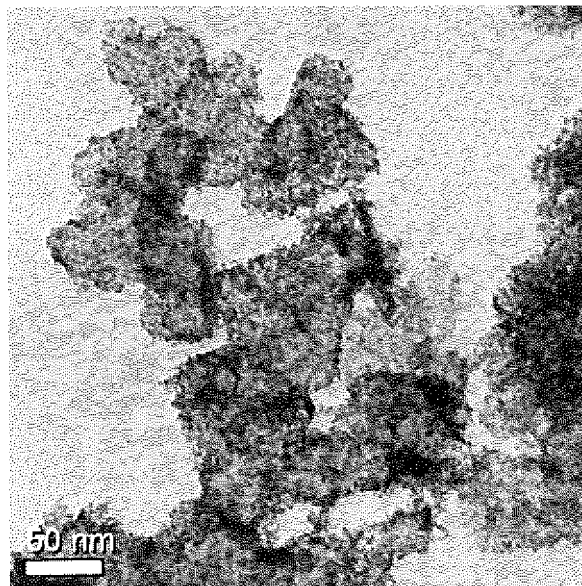


FIG. 10C

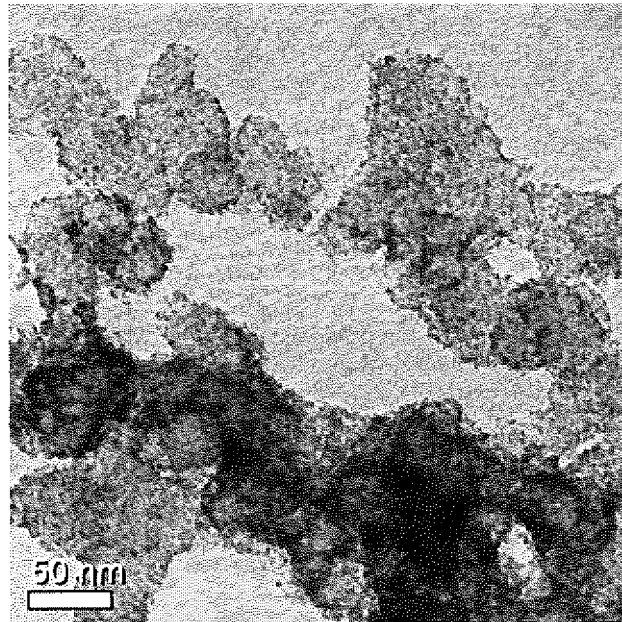


FIG. 10D

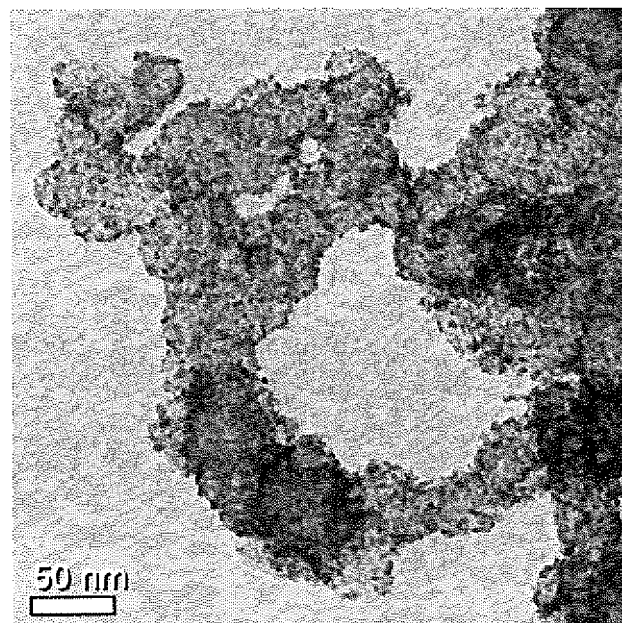


FIG. 11

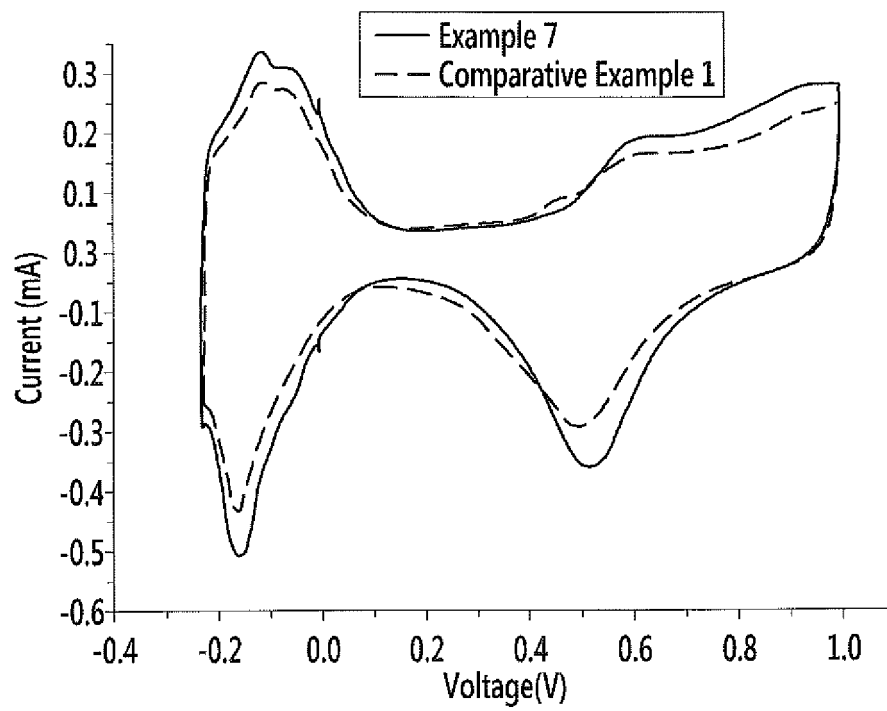


FIG. 12

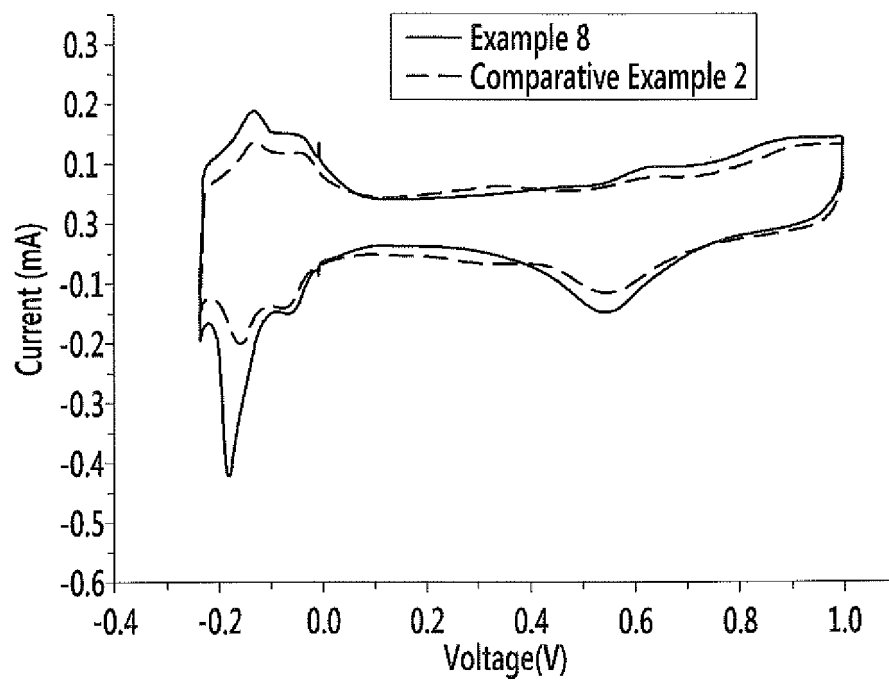


FIG. 13

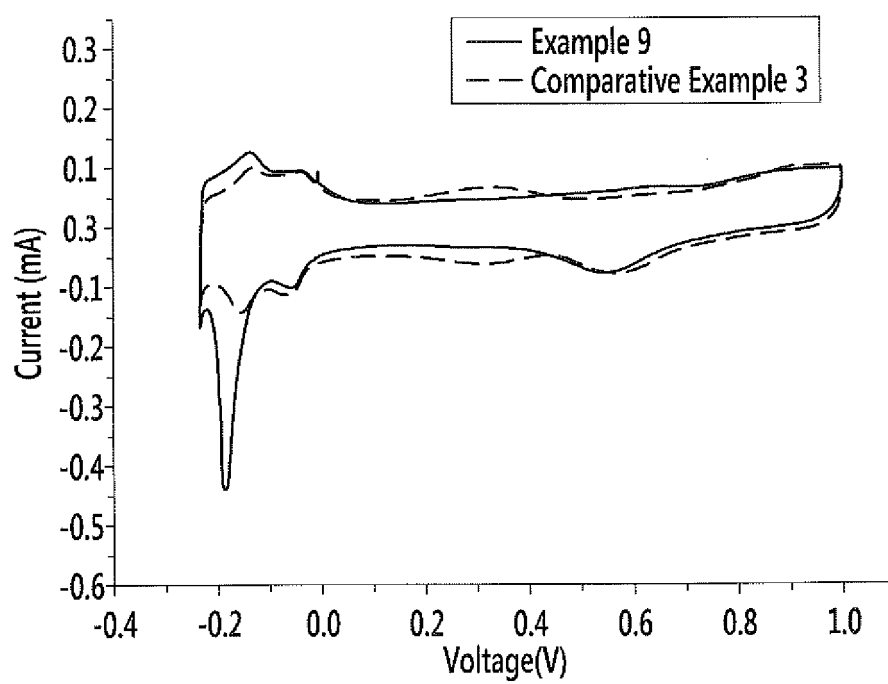


FIG. 14

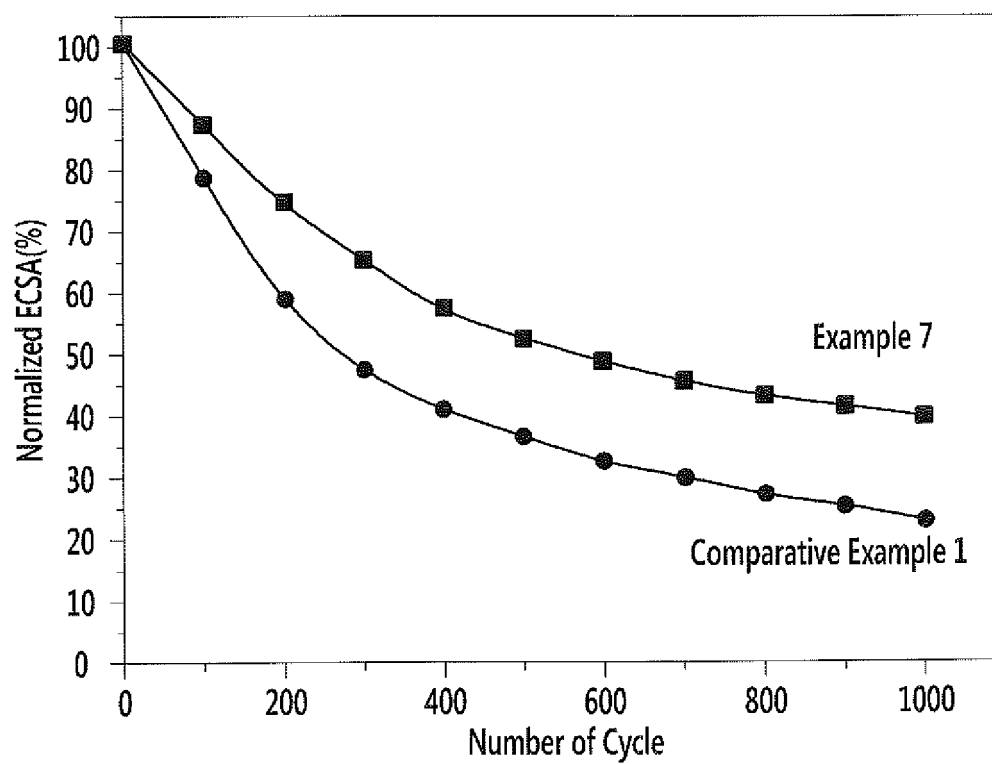


FIG. 15

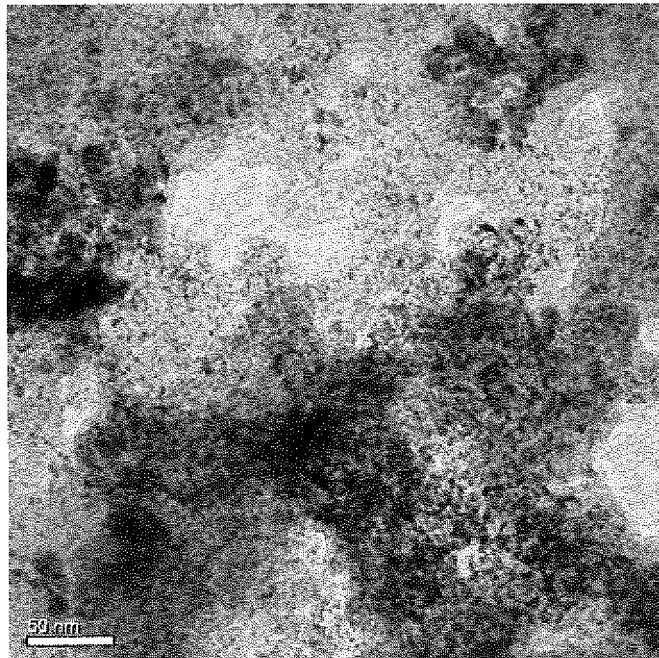
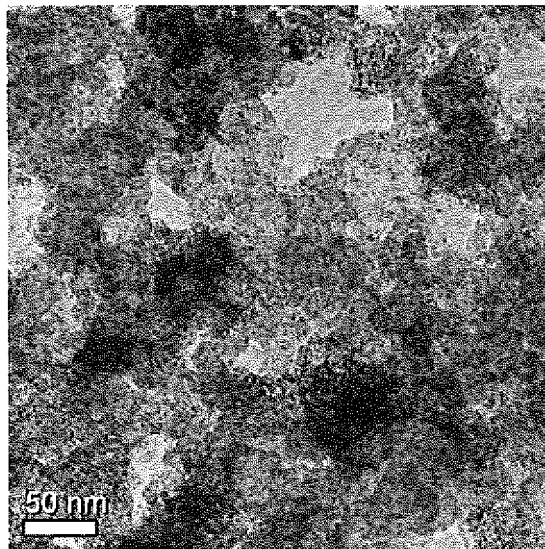


FIG. 16



REFERENCES CITED IN THE DESCRIPTION

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